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Intramolecular Arene C-H to C-P Functionalization Mediated by Ni(II) and Pd(II)

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Abstract

A trisphosphine ligand with a triarylbenzene backbone was employed to support mono-nickel(II) and palladium(II) complexes. Two phosphine arms coordinated to the metal center, while the third phosphine was found to form a C-P bond with dearomatization of the central arene. Deprotonation effected the rearomatization of the central ring and metal reduction from M(II) to M(0). The overall conversion corresponds to a functionalization of an unactivated arene C-H bond to a C-P bond. This transformation represents a rare type of mechanism of C-H functionalization, facilitated by the interactions of the group 10 metal with the arene π-system. This conversion is reminiscent of and expands the scope of recently reported intramolecular rearrangements of biaryl phosphine ligands common in group 10 catalysis.

The functionalization of C-H bonds catalyzed by transition metals has been an active field of research due to the potential applications in fine and commodity chemical synthesis, and petrochemical conversion.[1] Many metal-facilitated C-H functionalizations involve direct metal coordination or attack on the C-H moiety. This can take several forms: coordination of the C-H bond prior to oxidative addition, σ-bond metathesis, 1,2-addition, electrophilic aromatic metallation, or radical cleavage.[1a,1b,2] The oxidative addition mechanism as a common mode of C-H functionalization is shown in Figure 1a. For the functionalization of the C-H bonds of aromatic compounds, an alternative, extensively studied mechanism involves Cr and Mn η^6-arene complexes that are susceptible to nucleophilic attack (Figure 1b).[3] Subsequent oxidation leads to the rearomatization and release of functionalized arene. Arene elaboration upon strong binding of metals to part of the aromatic π-system has also been reported.[4] The latter two strategies for C-H functionalization require harsh conditions for metal removal due to strong metal-arene interactions.

Development of conceptually related chemistry with group 10 metals is appealing given the weaker metal-arene interactions and potential for metal removal under mild conditions conducive to catalyst turnover. Intramolecular C-H to C-C conversion has been recently reported for palladium coordinated biphenyl phosphines.[5] C-C bond formation with dearomatization was also observed for a nickel biphenyl phosphine complex.[6] The common property of these species is interaction of the metal center with arene leading to activation toward attack of the π-system. Herein, we present a rare example of C-H to C-P conversion

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Supporting Information. Detailed experimental procedures, characterization data, and crystallographic details for complexes **3a-Ni**, **4b-Ni**, **4b-Pd**, and **2c-Pd** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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with a mechanism for C-H functionalization unusual for group 10 metals, involving metal(II) activation of an arene π-system toward attack by a nucleophile (Figure 1c).

We have developed a family of bis- and trisphosphine ligands with terphenyl or triphenylbenzene linkers respectively, that support Ni complexes exhibiting metal-arene interactions.[7] To further explore the reactivity profile of such late metal-arene coordination complexes, we synthesized a modified trisphosphine **1a/b** (Scheme 1). Compounds **1a/b** contain a methylene group between the triarylbenzene and the phosphine moieties, which renders the framework more flexible compared to the related trisphosphine ligand[7c] with the phosphorus atoms directly bound to the outer aryl groups. Treatment of **1a/b** with one equivalent of $Pd(MeCN)_4(BF_4)_2$ (MeCN = acetonitrile) led to the formation of transient species, **2a/b-Pd**, that display two peaks in the ^{31}P NMR spectrum at 13.6 and 39.9 ppm in a 1:2 ratio. Structural characterization by single crystal X-ray diffraction studies (XRD) for **2a/b-Pd** were hindered by their instability. For comparison, the reaction of $Pd(MeCN)_4(BF_4)_2$ with a bisphosphine (**1c)** related to **1a/b** but missing one of the phosphine arms (Scheme S2) was investigated. A Pd(II) bisacetonitrile complex, **2c-Pd**, with the two phosphine donors coordinated in trans fashion (XRD, Figure S47) was isolated, and shows a single ^{31}P NMR signal at 39.7 ppm.[8] This is consistent with an assignment of **2a/b-Pd** as species with one free phosphine arm and two arms coordinating to Pd. Within 2 hours at room temperature, **2a/b-Pd** converted to new complexes **3a/b-Pd**, each with three peaks in the ^{31}P NMR spectrum. The ^{1}H NMR spectra of **3a/b-Pd** exhibit peaks in the olefinic region around 4.2 ppm. Treatment of **1a/b** with one equivalent of $Ni(OTf)_2$ (OTf = trifluoromethanesulfonate) generated complexes **3-Ni** that show ^{1}H NMR features similar to **3-Pd**. A single crystal X-ray diffraction (XRD) study of **3a-Ni** revealed a *C*1 Ni^{II} complex (Figure 2). The Ni center is coordinated to two phosphine arms (with P(1)–Ni–P(2) wide bite angle of 253°)[9] and presents short contacts (2.029(1)–2.118(1) Å) with three carbons of the central ring (Figure 2), consistent with an allyl-like bonding.[10] Most interestingly, one phosphine arm is now bonded to a carbon of the central ring. The sum of CCC and PCC angles (~329°) at C4 suggests an sp^3 carbon. NMR spectroscopy experiments (Figures S16–S18) allowed for identification of the signal at 3.8–4.2 ppm as the hydrogen on the central ring sp^3 carbon. Two of the central ring C-C bonds are longer than 1.55 Å, consistent with dearomatization. Additionally, the C5–C6 distance is shorter (1.360(1) Å), indicating an increased double bond character. Overall, these data suggest the formation of a phosphonium moiety. X-ray quality single crystals of **3-Pd** have not been obtained to date, but the NMR spectra are consistent with the analogous, structurally characterized **3-Ni**.

The dearomatization of the ring in compounds **3-Ni/Pd** is stabilized by the strong metal-allyl interaction. Although metal arene interactions were not observed in the precursors **2-Pd**, we propose that they are transient and activate the arene along the reaction pathway for nucleophilic attack by the phosphine. Interactions of group 10 metal(II) centers with arenes have been observed by crystallography, in particular for biaryl phosphines.[11] Recent reports of arene activation with C-C bond formation occur in intramolecular fashion as well. A Pd-facilitated reaction was proposed to occur via the insertion of an arene olefin moiety into a metal-aryl bond, as supported by the *syn* stereochemistry of the product.[5a,5b] In the present case, the pendant, free phosphine attacks the ring *anti* with respect to the metal center indicating that nucleophile coordination to the metal is not a prerequisite for attack on the ring. Hence, this provides an alternate mechanistic path for ring functionalization with heteroatom-based reagents, with potential for the development of intermolecular versions.

Treatment of compounds **3-Ni/Pd** with sodium acetate led to clean formation of new species. The ^{1}H NMR spectra suggest deprotonation at the central ring sp^3 position and rearomatization to generate **4-Ni/Pd** (Scheme 1). XRD studies of **4b-Ni/Pd** revealed a planar, aromatic central ring, in which the sum of CCC and PCC angles at C4 is 359°. The

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C–C distances of the central ring for **4b-Ni/Pd**, between 1.363(6) to 1.460(6) Å, depart slightly from aromaticity (Figure 2). This is due to the metal binding to one of the olefin moieties of the central arene, leading to partial localization of single and double bonds in the ring for which short and long C-C distances alternate.[7d] The Ni–C (1.986(6) and 2.020(6) Å) and Pd–C (2.183(4) Å) distances are consistent with M^0 oxidation state.[7a,12] Deprotonation hence leads to formal metal reduction from M^{II} to M^0.

The transition-metal mediated nucleophilic addition to arene double bond followed by deprotonation is effectively a C-H bond functionalization that leads to C-P bond formation in this case. To our knowledge, this is the first example of such a mechanism mediated by Ni^{II} and Pd^{II} without involving the formation of σ-complex or strong metal arene bonds (Scheme 1). Previously reported transition-metal-mediated dearomatization reactions via nucleophilic attack have been limited to d^6-complexes such as (η^6-arene)$Cr(CO)_3$ and [(η^6-arene)$Mn(CO)_3]^+$.[3,13] Rearomatization of the arene requires the presence of an anionic leaving group or stoichiometric chemical oxidation and metal loss, which has hindered the development of catalytic versions (Figure 1).[3a–c,3i] Our system is similar to the aforementioned such that the electrophilic, metal-coordinated arene moiety is susceptible to nucleophilic attack (Scheme 1). However, rearomatization to give the functionalized arene, with metal reduction, can be achieved by facile deprotonation due to the accessible M^0/M^{II} two electron couple for group 10 metals. Additionally, group 10 metals display relatively weak metal-arene interactions that, although strong enough to facilitate nucleophilic attack, are susceptible to arene exchange (after deprotonation) with potential for the development of catalytic versions of arene C-H functionalization.[14]

In summary, we have demonstrated a rare example of arene C-H functionalization mediated by Ni^{II} and Pd^{II} in an intramolecular fashion on a tris(phosphinoaryl)benzene framework. The Ni^{II} and Pd^{II} centers have been shown to promote nucleophilic attack on the central arene to yield a phosphonium moiety and dearomatization facilitated by the metal-allyl interaction. Deprotonation at the sp^3 carbon of these M^{II}-allyl complexes with base results in rearomatization and formal two-electron reduction of the metal center. The mechanism consistent with the present transformation has several attractive features stemming from the utilization of group 10 metals: activation of arene by weak metal-arene interactions, nucleophilic attack without metal coordination to nucleophile, and a facile M^0/M^{II} redox couple. With the current conceptual demonstration, future studies include the development of intermolecular versions of this transformation using various nucleophiles.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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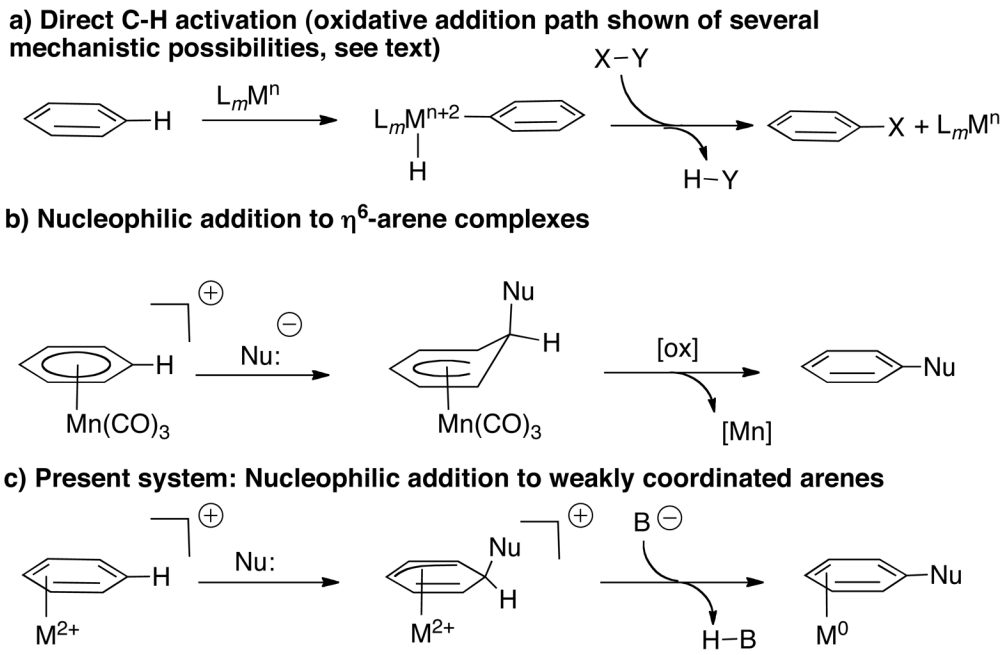

Figure 1.
Mechanisms of C-H activation

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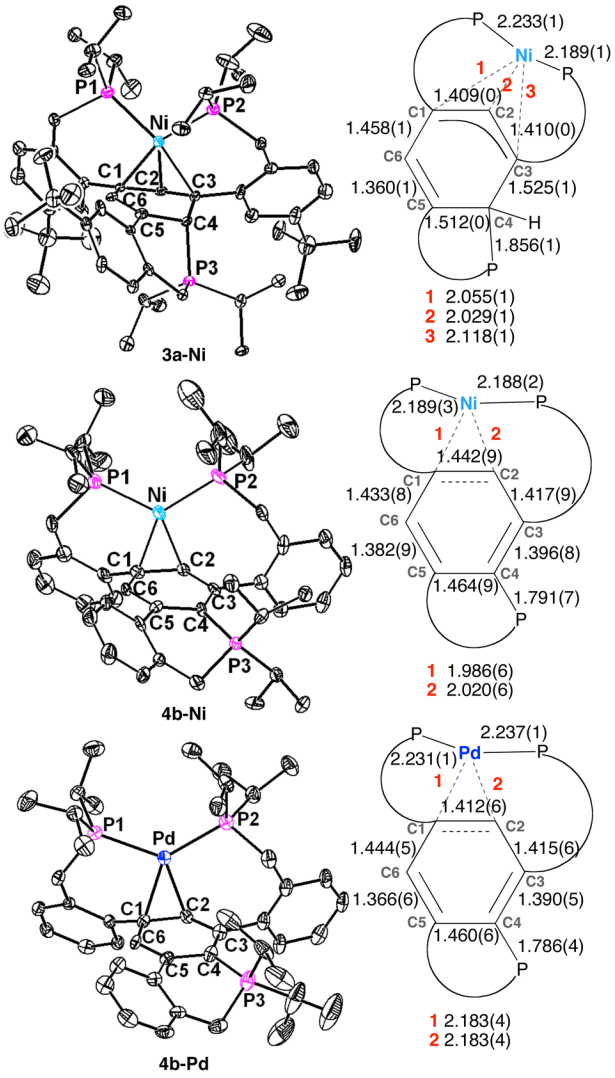
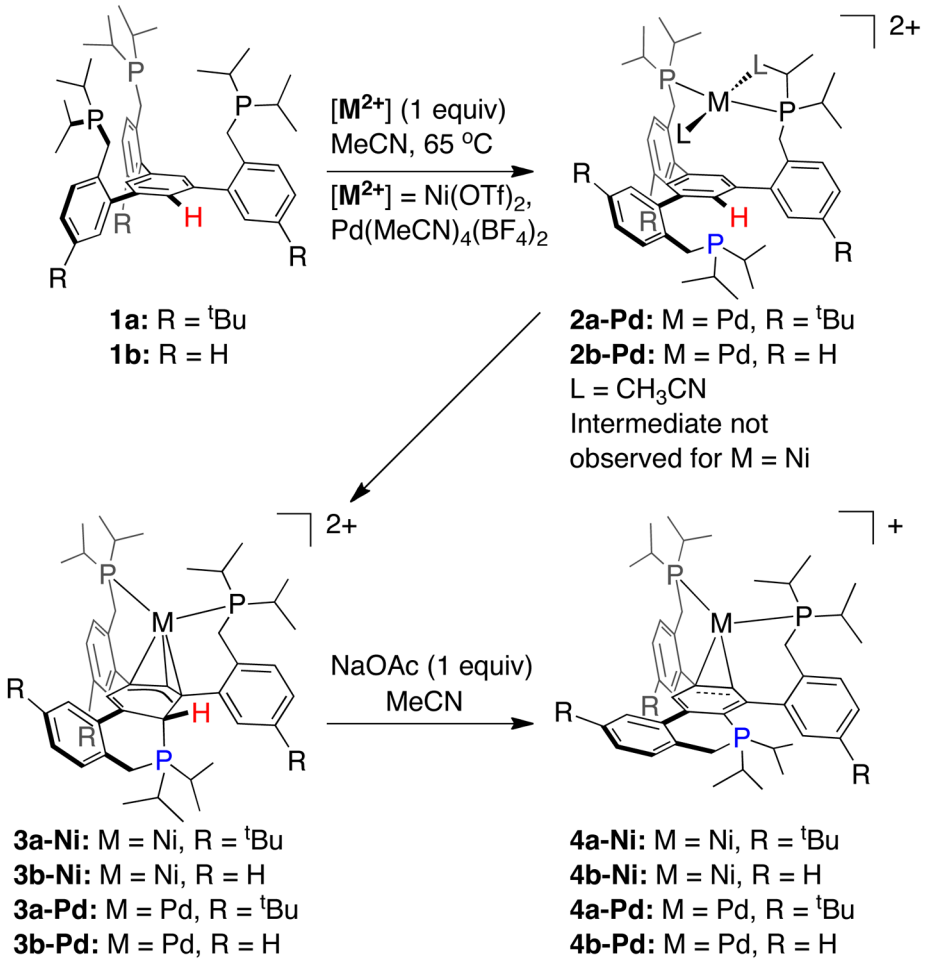


Figure 2.

Solid-state structures (left) and selected C–C, Ni–C, and M–P bond distances (Å, right) of **3a-Ni** (top), **4b-Ni** (middle), and **4b-Pd** (bottom). Hydrogen atoms and anions are omitted for clarity.



Scheme 1.
Synthesis of metal complexes and intramolecular C-H to C-P conversion

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